(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 907 800 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
19.08.2015 Bulletin 2015/34

(21) Application number: **13847667.6**

(22) Date of filing: **11.10.2013**

(51) Int Cl.:
C07C 31/135 *(2006.01)* ***C07C 29/149*** *(2006.01)*
C07B 61/00 *(2006.01)*

(86) International application number:
PCT/JP2013/077710

(87) International publication number:
WO 2014/061570 (24.04.2014 Gazette 2014/17)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **15.10.2012 JP 2012227838**

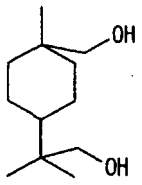
(71) Applicant: **Mitsubishi Gas Chemical Company, Inc.**
Tokyo 100-8324 (JP)

(72) Inventor: **KITAMURA, Mitsuharu**
Kurashiki-shi
Okayama 712-8525 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) NOVEL ALICYCLIC-TYPE DIOL COMPOUND, AND METHOD FOR PRODUCING SAME

(57) The alicyclic diol compound of the present invention is represented by the following formula (1).



(1)

EP 2 907 800 A1

Description

Technical Field

[0001] The present invention relates to a new alicyclic diol compound having a cyclohexane ring, and a manufacturing method thereof.

Background Art

[0002] A polyester resin synthesized from an alicyclic dicarboxylic acid and an alicyclic diol can be applied to use as optical materials, electronic information materials, and medical appliance materials, due to excellence in transparency, heat resistance, weather resistance, gas barrier property, and optical properties.

[0003] For example, using 1,4-cyclohexane dicarboxylic acid (1,4-CHDA) as alicyclic dicarboxylic acid, and 1,4-cyclohexane dimethanol (1,4-CHDM) as alicyclic diol, a polyester resin excellent in biodegradability (refer to, for example, Patent Document 1), a conductive polyester emitting a less amount of gas (refer to, for example, Patent Document 2), and a polyester having a short foam-disappearing time, suitable for use in medical application (refer to, for example, Patent Document 3) are synthesized. Furthermore, using tricyclo[3.3.1.$1^{3,7}$]decane dicarboxylic acid as alicyclic dicarboxylic acid, and tricyclo[3.3.1.$1^{3,7}$]decane diol as alicyclic diol, a polyester resin having small optical anisotropy, excellent in moldability, is synthesized (refer to, for example, Patent Document 4).

List of Prior Art Documents

Patent Document

[0004]

Patent Document 1
Japanese Patent Laid-Open No. 2000-290356
Patent Document 2
Japanese Patent Laid-Open No. 2004-124022
Patent Document 3
Japanese Patent Laid-Open No. 2005-298555
Patent Document 4
Japanese Patent No. 3862538

Summary of Invention

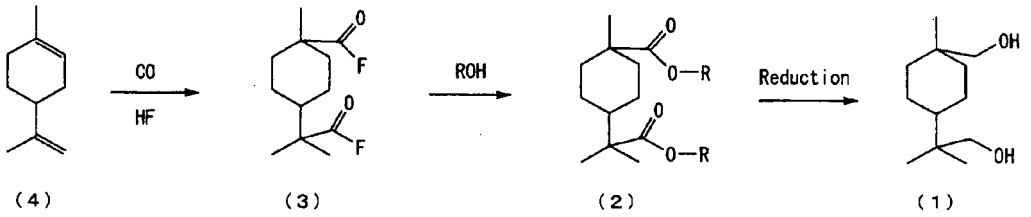
Problems to be Solved by Invention

[0005] An object of the present invention is to provide a new alicyclic diol compound having a cyclohexane ring and a manufacturing method thereof.

Means for Solving Problems

[0006] The present inventor has investigated a method of manufacturing a new alicyclic diol compound represented by the following formula (1) from 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4), and found out that the new alicyclic diol compound represented by the following formula (1) can be manufactured by, for example, reacting 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4) with carbon monoxide in the presence of hydrogen fluoride (hereinafter also referred to as "HF"), subsequently reacting the produced alicyclic dicarboxylic acid fluoride represented by the following formula (3) with alcohol so as to produce an alicyclic dicarboxylic acid ester compound represented by the following formula (2), and then reducing the alicyclic dicarboxylic acid ester compound represented by the following formula (2).

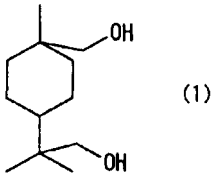
[0007] The present invention has been thus accomplished based on the finding.



wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

[0008] Specifically, the present invention is described as follows.

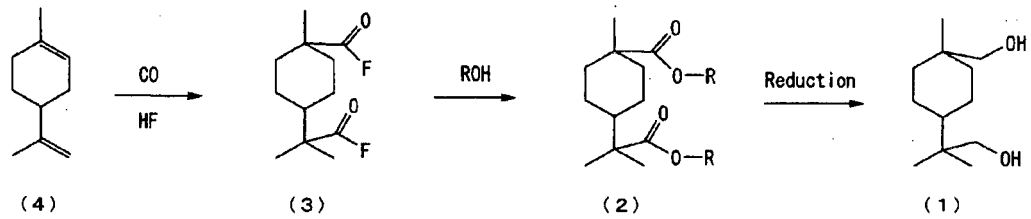
[1] An alicyclic diol compound represented by the following formula (1).



(1)

[2] A method of manufacturing an alicyclic diol compound comprising the steps of:

reacting 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4) with carbon monoxide in the presence of hydrogen fluoride so as to produce an alicyclic dicarboxylic acid fluoride represented by the following formula (3);
reacting the produced alicyclic dicarboxylic acid fluoride represented by the following formula (3) with alcohol so as to produce an alicyclic dicarboxylic acid ester compound represented by the following formula (2); and
reducing the produced alicyclic dicarboxylic acid ester compound represented by the following formula (2) so as to produce a new alicyclic diol compound represented by the following formula (1):



wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

Advantages of Invention

[0009] The new alicyclic diol compound represented by the formula (1) of the present invention can be used, for example, as a raw material of polyester resins. Since the manufacturing method of the present invention uses a compound represented by the formula (4) derived from biomass as a raw material, it can be said that the manufacturing method is environment-friendly in terms of carbon neutrality.

Brief Description of Drawings

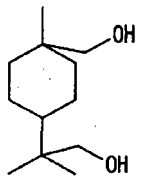
[0010]

[Figure 1] Figure 1 is a chart showing DEPT 45°-NMR measurement results of a product obtained in Example 1.
[Figure 2] Figure 2 is a chart showing DEPT 90°-NMR measurement results of a product obtained in Example 1.
[Figure 3] Figure 3 is a chart showing DEPT 135°-NMR measurement results of a product obtained in Example 1.
[Figure 4] Figure 4 is a chart showing Carbon i.g.-NMR measurement results of a product obtained in Example 1.
[Figure 5] Figure 5 is a chart showing INADEQUATE-NMR measurement results of a product obtained in Example 1.
[Figure 6] Figure 6 is an enlarged chart showing measurement results in a portion from 15 to 50 ppm in Figure 5.

Mode for Carrying Out Invention

[0011] The embodiments of the present invention (hereinafter also referred to as "the present embodiment") are described in detail in the following. The following embodiments are, however, provided to illustrate the present invention, and the present invention is not limited thereto only.

[0012] The new alicyclic diol compound of the present embodiment is a compound represented by the following formula (1).

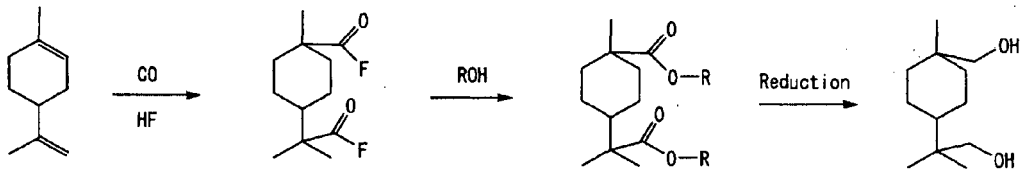


(1)

[0013] The alicyclic diol compound represented by the formula (1) may be used, for example, as a raw material for polyester resins, and a material excellent in optical properties and heat resistance can be manufactured by using the alicyclic diol compound. Examples of the application of the material having such properties include, but not particularly limited to, optical materials such as lenses.

[0014] The method of manufacturing the new alicyclic diol compound of the present embodiment comprises the following steps (a) to (c):

(a) A step of reacting 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4) with carbon monoxide in the presence of hydrogen fluoride (hereinafter also referred to as "HF") so as to produce an alicyclic dicarboxylic acid fluoride represented by the following formula (3)(hereinafter sometimes abbreviated as "carbonylation step");
(b) A step of reacting the produced alicyclic dicarboxylic acid fluoride represented by the following formula (3) with alcohol so as to produce an alicyclic dicarboxylic acid ester compound represented by the following formula (2) (hereinafter sometimes abbreviated as "esterification step"); and
(c) A step of reducing the produced alicyclic dicarboxylic acid ester compound represented by the following formula (2) so as to produce an alicyclic diol compound represented by the following formula (1) (hereinafter sometimes abbreviated as "reduction step").

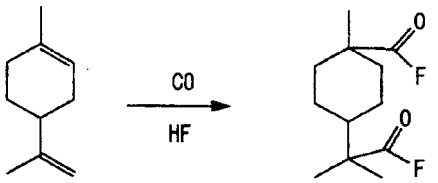


(4) (3) (2) (1)

wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

<(a) Carbonylation step>

[0015] In the step (a), the carbonylation reaction of 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4) is preferably performed in the presence of HF under pressure of carbon monoxide. Through the step (a), an alicyclic carbonyl compound represented by the following formula (3) (hereinafter also referred to as "alicyclic dicarboxylic acid fluoride") is produced. The product of the carbonylation reaction in the step (a) may contain various by-products (containing other isomers).



(4) (3)

[Carbon monoxide]

[0016] The carbon monoxide for use in the carbonylation step may contain an inert gas such as nitrogen and methane. The carbonylation step is performed under a carbon monoxide partial pressure in the range of preferably 0.5 to 5 MPa, more preferably 1 to 4 MPa, furthermore preferably 1.5 to 3 MPa. Under a carbon monoxide partial pressure of more than 0.5 MPa, the carbonylation reaction proceeds sufficiently without concurrence of side reactions such as disproportionation and polymerization, so that the target substance, i.e. alicyclic dicarboxylic acid fluoride, can be obtained at a high yield. A carbon monoxide partial pressure of 5 MPa or less is preferred, considering the load on equipment.

[Hydrogen fluoride]

[0017] Since HF for use in the carbonylation step functions as a solvent, a catalyst, and a secondary raw material for the reaction, use of substantially anhydrous HF is preferred. In the present embodiment, the substantially anhydrous HF means HF with a water concentration of 200 ppm or less. In the carbonylation step, the amount of HF for use is preferably 4 to 30 times by mole, more preferably 7 to 20 times by mole, furthermore preferably 10 to 15 times by mole, as large as the amount of raw material 4-isopropenyl-1-methyl-1-cyclohexene. With an amount of HF for use of 4 times by mole or more, the carbonylation reaction proceeds efficiently, with concurrence of side reactions such as disproportionation and polymerization being suppressed, so that the target substance, i.e. alicyclic dicarboxylic acid fluoride, can be obtained at a high yield. The amount of HF for use is preferably 30 times by mole or less, more preferably 15 times by mole or less, considering raw material costs and productivity.

[Reaction conditions]

[0018] The type of carbonylation reaction in the step (a) is not particularly limited. Any of a batch type, a semi-continuous type, a continuous type, and the like may be employed.

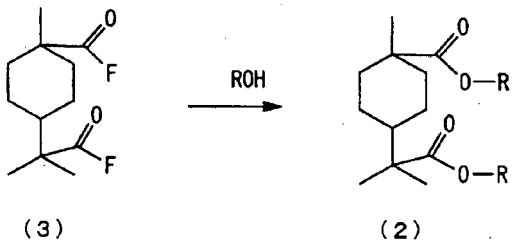
[0019] The reaction temperature of carbonylation reaction in the step (a) is preferably in the range of -50°C to 30°C, more preferably -40°C to 0°C, furthermore preferably -30 to -10°C. At a reaction temperature of the carbonylation reaction of 30°C or less, in particular - 10°C or less, improved selectivity tends to be achieved. The carbonylation reaction in the step (a) is preferably performed at -50°C or more, considering the reaction rate.

[0020] The reaction pressure of carbonylation reaction in the step (a) is preferably in the range of 0.6 to 5.0 MPa, more preferably 1.1 to 4.0 MPa, furthermore preferably 1.6 to 3.0 MPa.

<(b) Esterification step>

[0021] The esterification step is a step of reacting the alicyclic dicarboxylic acid fluoride produced in the carbonylation step with an alcohol having 1 to 4 carbon atoms so as to produce an alicyclic dicarboxylic acid ester compound. In the esterification step, the reaction liquid produced in the carbonylation step may be directly used. Considering the corrosivity of a reaction apparatus, in the esterification step, a method in which a predetermined amount of alcohol is added to the reaction liquid produced in the carbonylation step is preferred. Alternatively, an excessive amount of HF may be distilled away from the reaction liquid produced in the carbonylation step and then alcohol may be added to the reaction liquid for esterification.

[0022] Instead of using the reaction liquid of acid fluoride produced in the carbonylation reaction in the esterification step: (I) after distilling excessive amount of HF away, the reaction liquid may be refined by a conventional method such as distillation, so that the acid fluoride can be directly used as a raw material in the subsequent reduction step; or (II) after distilling excessive amount of HF away, the reaction liquid may be hydrolyzed to produce a corresponding carboxylic acid, which is refined by a conventional method such as distillation, so that the carboxylic acid can be used as a raw material in the subsequent reduction step.



wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

[0023] Specific examples of the alcohol for use in the esterification step include methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol, isobutyl alcohol, and tert-butyl alcohol, though not being particularly limited. Among them, methanol or ethanol is preferred, considering the reactivity. In the esterification step, one type of alcohol may be used alone or two or more types may be used in combination.

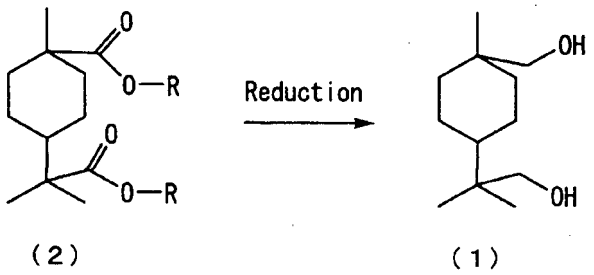
[0024] The amount of alcohol for use in the esterification step is preferably 1.0 to 2.5 times by mole, more preferably 1.2 to 2.3 times by mole, furthermore preferably 1.5 to 2.0 times by mole, as large as the amount of raw material 4-isopropenyl-1-methyl-1-cyclohexene in the carbonylation step. With an amount of alcohol for use of 1.0 times by mole or more, the remaining amount of unreacted alicyclic dicarboxylic acid fluoride is small, resulting in little corrosion of apparatus in a subsequent step, which is preferable. An amount of alcohol for use of 2.5 times by mole or less is preferred, from the viewpoint of suppressing the corrosion of apparatus by water produced in an intermolecular dehydration reaction of alcohol.

[0025] The reaction temperature in the esterification step is preferably -40°C or more and 20°C or less, more preferably -30°C to 10°C, furthermore preferably -30°C to 0°C, from the viewpoint of suppressing decomposition of the alicyclic dicarboxylic acid ester compound represented by the above formula (2). With a reaction temperature of -40°C or more, the esterification rate can be accelerated to improve the yield. With a reaction temperature of 20°C or less, the decomposition of ester can be suppressed and by-product water due to dehydration reaction of alcohol can be suppressed.

[0026] The esterification step is preferably performed under normal pressure.

<(c) Reduction step>

[0027] In the step (c), the method for reducing the alicyclic dicarboxylic acid ester compound represented by the formula (2) (hereinafter also referred to as "alicyclic dicarboxylic acid ester compound") produced in the esterification step may be any of the conventional method for reducing a carbonyl compound to alcohol, without particular limitations. The reduction method for use may be, for example, any of hydride reduction, reduction using a metal and a metal salt, and reduction by catalytic hydrogenation, which are described in The Fifth Series of Experimental Chemistry Vol. 14 (Maruzen) pp. 11-27. Among them, reduction by catalytic hydrogenation is preferred from the viewpoint of economic efficiency.



wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

[Catalytic hydrogenation catalyst]

[0028] Although the catalyst for use in catalytic hydrogenation of an alicyclic dicarboxylic acid ester compound (hereinafter also referred to as "catalytic hydrogenation catalyst") is not particularly limited as long as being a conventional catalysts for use in hydrogenation of a carbonyl compound, preferably the catalyst includes at least one selected from metals in groups 8 to 11 of the periodic table.

[0029] Specific examples of the catalytic hydrogenation catalyst include a catalytic hydrogenation catalyst which contains at least one selected from iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium,

platinum, and gold, though not being particularly limited.

[0030] Although the catalytic hydrogenation catalyst may be a solid catalyst or a homogeneous catalyst, a solid catalyst is preferred considering the isolation from reaction products. Examples of the solid catalyst include an unsupported metal catalyst and a supported metal catalyst, though not being particularly limited.

[0031] Preferred examples of the unsupported metal catalyst include a Raney catalyst such as Raney nickel, Raney cobalt, and Raney copper, an oxide of platinum, palladium, rhodium, ruthenium, or the like, and a colloidal catalyst.

[0032] Examples of the supported metal catalyst include a supported metal catalyst composed of at least one of iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold supported on or blended with a carrier such as magnesia, zirconia, ceria, diatomaceous earth, activated carbon, alumina, silica, zeolite, or titania, though not being particularly limited. Among them, a supported copper catalyst such as a copper-chromium catalyst (Adkins catalyst), a copper-zinc or copper-iron catalyst, a supported platinum catalyst such as Pt/C and Pt/alumina, a supported palladium catalyst such as Pd/C and Pd/alumina, a supported ruthenium catalyst such as Ru/C and Ru/alumina, or a supported rhodium catalyst such as Rh/C and Rh/alumina is preferred. Among these, a catalyst which contains at least one selected from the group consisting of nickel and copper is more preferred in terms of the reaction activity.

[0033] In the reduction step, the amount of catalytic hydrogenation catalyst for use is preferably 1 to 100 parts by mass, more preferably 3 to 30 parts by mass, furthermore preferably 5 to 20 parts by mass, relative to 100 parts by mass of the raw material alicyclic dicarboxylic acid ester compound, though depending on the type of catalyst.

[Solvent]

[0034] The reduction step can be performed without solvent. Alternatively, a solvent may be used in the step.

[0035] Examples of the solvent for use in the reduction step include water; organic acids such as formic acid and acetic acid; aromatic compounds such as benzene, o-dichlorobenzene, toluene, and xylene; hydrocarbons such as hexane, heptane, and cyclohexane; alcohols such as methanol, ethanol, isopropyl alcohol, t-butyl alcohol, ethylene glycol and diethylene glycol; ethers such as dioxane, tetrahydrofuran, dimethoxyethane, and diglyme; or a mixture thereof; though not being particularly limited. Among them, solvent-free; aromatic compounds such as benzene, o-dichlorobenzene, toluene, and xylene; hydrocarbons such as hexane, heptane, and cyclohexane; alcohols such as methanol, ethanol, isopropyl alcohol, t-butyl alcohol, ethylene glycol, and diethylene glycol; ethers such as dioxane, tetrahydrofuran, dimethoxyethane, and diglyme; or a mixture thereof, is preferably employed.

[0036] In the reduction step, the amount of solvent for use is preferably 0 to 30 times by mass, more preferably 0 to 20 times by mass, furthermore preferably 0 to 10 times by mass, as large as the amount of alicyclic dicarboxylic acid ester compound represented by the formula (2) produced in the esterification step.

[Reaction conditions]

[0037] A higher hydrogen pressure in the reduction step is more preferred for shifting the reaction equilibrium to the alcohol side. The pressure is preferably 1 to 30 MPa, more preferably 5 to 25 MPa, furthermore preferably 10 to 20 MPa, considering equipment cost.

[0038] The reaction temperature in the reduction step is preferably 100°C or more, more preferably 150°C or more, furthermore preferably 180°C or more, from the viewpoint of obtaining a sufficient reaction rate. The reaction temperature in the reduction step is preferably 300°C or less, more preferably 290°C or less, furthermore preferably 280°C or less, from the viewpoint of suppressing the transesterification reaction between an alicyclic diol compound represented by the formula (1) to be produced and an alicyclic dicarboxylic acid ester compound represented by the formula (2).

[0039] The reaction pressure in the reduction step is in the range of preferably 1.5 to 30 MPa, more preferably 6 to 25 MPa, furthermore preferably 10 to 20 MPa.

[0040] The type of reduction step is not particularly limited. For example, in the case of reduction by catalytic hydrogenation, the type of reduction step is not particularly limited as long as the catalytic hydrogenation reaction is feasible, so that a known, commonly used type may be employed. Examples of the reactor in which the reduction step is performed include a suspended bed reactor for performing catalytic hydrogenation reaction with catalysts fluidized in a fluid, and a fixed bed reactor filled with catalysts to be fixed for performing catalytic hydrogenation reaction by supplying a fluid, though not being particularly limited.

[0041] In the reduction step, alcohols having 1 to 4 carbon atoms may be by-produced during the reaction in some cases. The reduction step may be performed with the by-products remaining, or may be performed with the by-products being continuously or intermittently removed during the reaction.

<Other steps>

[0042] The manufacturing method of the present embodiment may comprise other steps other than the steps (a) and

(b) described above. Examples of the other step include a liquid-liquid extraction step, a catalyst recovery step, a neutralization and washing step, an auxiliary agent recovery step, and a refining step, though not being particularly limited.

[0043] Examples of the refining step include: a step of, after distilling HF away from the reaction liquid containing an alicyclic dicarboxylic acid ester compound represented by the formula (2) produced in the esterification step, refining the reaction liquid by a conventional method such as distillation; and a step of, after separating the hydrogenation catalyst from the products containing the alicyclic diol compound represented by the formula (1) produced in the reduction step, refining the products by a conventional method such as distillation and recrystallization; though not being particularly limited. Through such a refining step, a new high-purity alicyclic diol represented by the formula (1) can be obtained.

Examples

[0044] Hereinafter, the present invention will be specifically described with reference to Examples, but the present invention is not intended to be limited to these examples. Unless otherwise specified, "%" in the following means mass%.

<Analytical method and conditions>

[Analysis conditions for gas chromatography]

[0045] In gas chromatography, a measurement apparatus GC-17A made by SHIMADZU CORPORATION and a capillary column HR-1 made by ULBON (0.32 mmϕ $\times$ 25 m $\times$ 0.50 μm) were used. The temperature-rising conditions were set such that the temperature was raised from 100°C to 300°C at a rate of 5°C/min.

[Yield and isomer ratio of dicarboxylic acid ester compound]

[0046] By gas chromatography analysis, the area ratios (GC%) of several types of isomeric dicarboxylic acid ester compounds as products were obtained, and the yield and the isomer ratio of the dicarboxylic acid ester compounds were calculated by an internal reference method using the following expression.

[0053]

$$\{\text{Yield of dicarboxylic acid ester compound (mol\%)}\} = \{\text{Total acquisition mass of dicarboxylic acid ester compound}/256.3\}/\{\text{Raw material feed mass}/136.2\} \times 100$$

[0054]

$$\{\text{Isomer ratio (\%)}\} = \{\text{Methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate (GC\%)}\}/\{\text{Total of dicarboxylic acid ester compounds (GC\%)}\} \times 100$$

[0047] The isomer in the description means a structural isomer having a carbonyl group at a different insertion position.

[Yield of alicyclic diol compounds]

[0048] By gas chromatography analysis, the area ratios (GC%) of several types of isomeric diol compounds as products were obtained, and the yield of 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol was calculated by an internal reference method.

[GC-MS]

[0049] As GC-MS measurement apparatus, a GC-MS spectrometer POLARIS Q made by Thermo ELECTRON Corporation was used.

[NMR]

[0050] NMR was measured under the following conditions.

Apparatus: Bruker Avance 600II (600 MHz-NMR)
Mode: Proton, Carbon, DEPT 45°, 90°, and 135°, Carbon i.g., and INADEQUATE
Solvent: CDCl3 (deuterated chloroform)
Internal reference substance: tetramethylsilane

<Example 1>

[0051] Manufacturing of methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate ((a) Carbonylation step and (b) Esterification step)

4-isopropenyl-1-methyl-1-cyclohexene

methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate

[Carbonylation step]

[0052] Using a stainless steel autoclave with an internal volume of 500 ml including a Nack drive type stirrer and three inlet nozzles at the top and one extraction nozzle at the bottom, with a jacket for internal temperature control, the carbonylation step was performed as follows.

[0053] First, the atmosphere in the autoclave was substituted with carbon monoxide. Subsequently, 230 g (11.5 mol) of anhydrous hydrogen fluoride was introduced into the autoclave, and the liquid temperature in the autoclave was set to -27°C. The inside of the autoclave was then pressurized to 2 MPa with carbon monoxide.

[0054] In the autoclave with the reaction temperature being kept at -27°C, and the reaction pressure being kept at 2 MPa, 104.4 g (0.77 mol) of 4-isopropenyl-1-methyl-1-cyclohexene was supplied from the top of the autoclave, so that the carbonylation reaction was performed. After completion of the supply, with stirring of the reaction liquid being continued for about 10 minutes until no absorption of carbon monoxide was observed, an alicyclic dicarboxylic acid fluoride was thereby obtained.

[Esterification step]

[0055] Subsequently, in the autoclave with the reaction temperature being kept at -27°C, 49.1 g (1.53 mol) of methanol was supplied from the top of the autoclave, so that esterification of the alicyclic dicarboxylic acid fluoride was performed with the reaction liquid being stirred for 1 hour.

[0056] The reaction liquid was extracted from the bottom of the autoclave into ice water, so that an oil phase and an aqueous phase were separated. Subsequently, the oil phase was washed twice with 100 ml of 2% caustic soda aqueous solution and twice with 100 ml of distilled water, and was dehydrated with 10 g of anhydrous sodium sulfate. After dehydration, the produced liquid was analyzed by gas chromatography. As a result, the yield of the dicarboxylic acid ester compound was 26.6 mol% (on 4-isopropenyl-1-methyl-1-cyclohexene basis), and the yield of methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate was 21.1 mol% (on 4-isopropenyl-1-methyl-1-cyclohexene basis, isomer ratio: 79.2%).

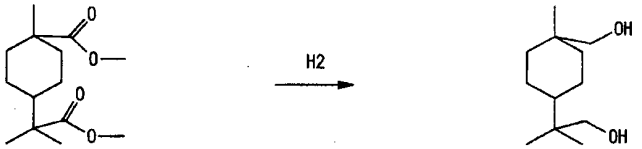
[Isolation and refining of esterification reaction product]

[0057] By reduced-pressure distillation of the liquid produced in the esterification step with an evaporator, low-boiling point substances were removed from the liquid. Subsequently, the low-boiling point substance-removed liquid was rectified using a rectification column with a theoretical plate number of 20 (distillation temperature: 177°C, degree of vacuum: 20 torr). Through the rectification, 42.0 g of a product as main fraction having an isomer ratio of 92.0% by gas chromatography analysis (distilled yield: 93.2 mol%, on methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate basis) was obtained.

[Reduction step]

Manufacturing of 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol

[0058]



methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate

2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol

[0059] In an stainless steel autoclave, 3.0 g of a copper-zinc catalyst supported on alumina (made by JGC Catalysts and Chemicals Ltd.) and 30.0 g of the product produced as main fraction in the isolation and refining (containing methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate with an isomer ratio of 92.0% and other isomers in an amount of 8.0%) were placed, and the mixture was stirred for 15 hours at 280°C, under a hydrogen pressure of 15 MPa, in a solvent-free state with hydrogen passing. The reduction reaction of methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate was thus performed.

[0060] The catalyst was removed by filtering the reaction liquid, so that 19.1 g of a product (mixture) was manufactured, containing 0.8% of methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate, 9.6% of perhydrogenated product, 89.0% of 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol, and 0.6% of other isomers. The yield of 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol was 78.9 mol% (on methyl-4-(1-methoxy-2-methyl-1-oxopropan-2-yl)-1-methylcyclohexane carboxylate basis).

[Recrystallization refining of reduction reaction product]

[0061] The product obtained in the reduction step was dissolved in methanol. Subsequently, 40 g of n-hexane was slowly poured into the produced solution, and the precipitated crystals were separated by filtration. The obtained product was a white solid with a purity of 100% (12.6 g, crystallization yield: 65.7 mol%, on 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol basis).

<Product identification>

[0062] As a result of GC-MS analysis, the product obtained in the recrystallization refining in Example 1 had a molecular weight of 200.

[0063] Using the NMR apparatus, 1H-NMR measurement, 13C-NMR measurement, DEPT 45°, 90°, and 135°-NMR measurement, Carbon i.g.-NMR measurement, and INADEQUATE-NMR measurement were performed. The results of 1H-NMR measurement and 13C-NMR measurement are shown as follows, and the results of DEPT 45°, 90°, and 135°-NMR measurement, Carbon i.g.-NMR measurement, and INADEQUATE-NMR measurement are shown in Figure 1 to Figure 6.

[NMR measurement results of product obtained in Example 1]

[0064] 1H-NMR (600 MHz, CDCl3, TMS, ppm) δ: 0.700-0.955 (m, 9H), 1.113-1.231 (m, 6H), 1.473-1.560 (m, 2H), 1.638-1.726 (m, 2H), 3.281-3.457 (m, 4H), 4.907 (m, 1H)

[0065] 13C-NMR (600 MHz, CDCl3, TMS, ppm) δ: 22.27, 23.29, 28.22, 35.07, 36.02, 37.86, 43.94, 49.01, 66.64, 70.60

[0066] Figure 1 is a chart showing DEPT 45°-NMR measurement results. From Figure 1, it was found that the fourth and sixth peaks for quaternary carbon atoms were missing. Figure 2 is a chart showing DEPT 90°-NMR measurement results. From Figure 2, it was found that the seventh peak for a tertiary carbon atom was strongly detected. Figure 3 is a chart showing DEPT 135°-NMR measurement results. It was found that the second, fifth, eighth, and ninth peaks for secondary carbon atoms were detected in the downward direction. Figure 4 is a chart showing Carbon i.g.-NMR measurement results. From Figure 4, the number of carbon was confirmed. Figure 5 and Figure 6 are charts showing INADEQUATE-NMR measurement results (Figure 6 is an enlarged chart showing measurement results in a portion for 15 to 50 ppm in Figure 5.). From Figure 5 and Figure 6, the correlations of direct bonding between carbons were elucidated.

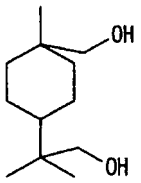
[0067] Based on comprehensive determination from the measurement results, the main component of the product obtained in Example 1 was identified to be 2-(4-(hydroxymethyl)-4-methylcyclohexyl)-2-methylpropan-1-ol.

Industrial Applicability

[0068] The new alicyclic diol compound obtained in the present invention is useful as various industrial chemical raw materials and raw materials for manufacturing functional optical materials and functional electronic materials.

Claims

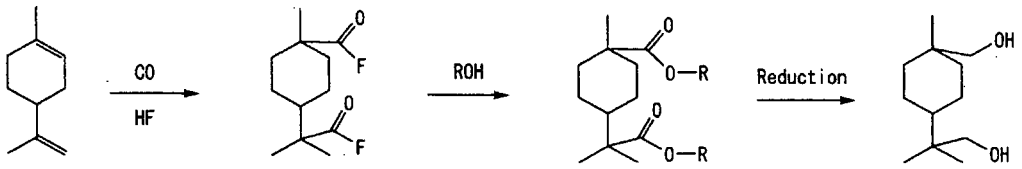
1. An alicyclic diol compound represented by the following formula (1).



(1)

2. A method of manufacturing an alicyclic diol compound comprising the steps of:

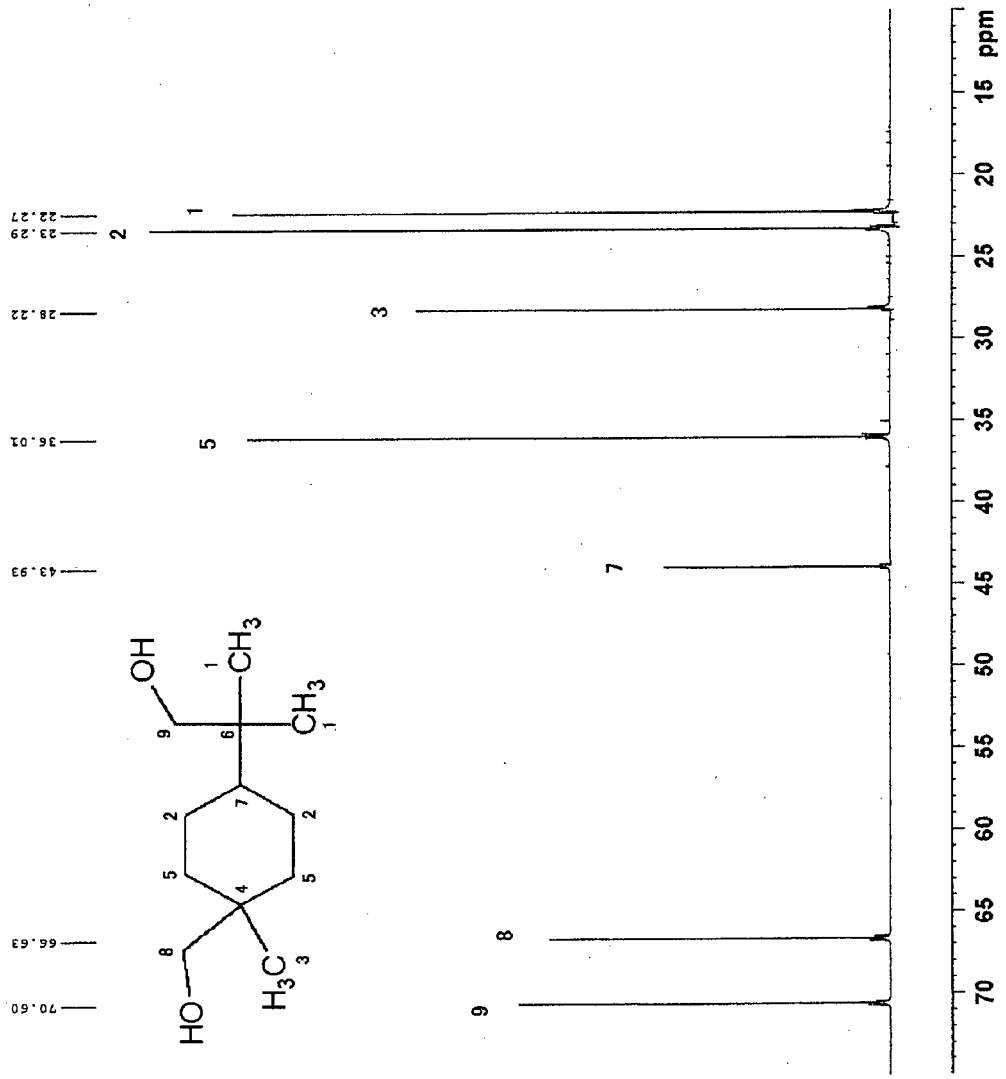
reacting 4-isopropenyl-1-methyl-1-cyclohexene represented by the following formula (4) with carbon monoxide in the presence of hydrogen fluoride so as to produce an alicyclic dicarboxylic acid fluoride represented by the following formula (3);
reacting the produced alicyclic dicarboxylic acid fluoride represented by the following formula (3) with alcohol so as to produce an alicyclic dicarboxylic acid ester compound represented by the following formula (2); and
reducing the produced alicyclic dicarboxylic acid ester compound represented by the following formula (2) so as to produce an alicyclic diol compound represented by the following formula (1):



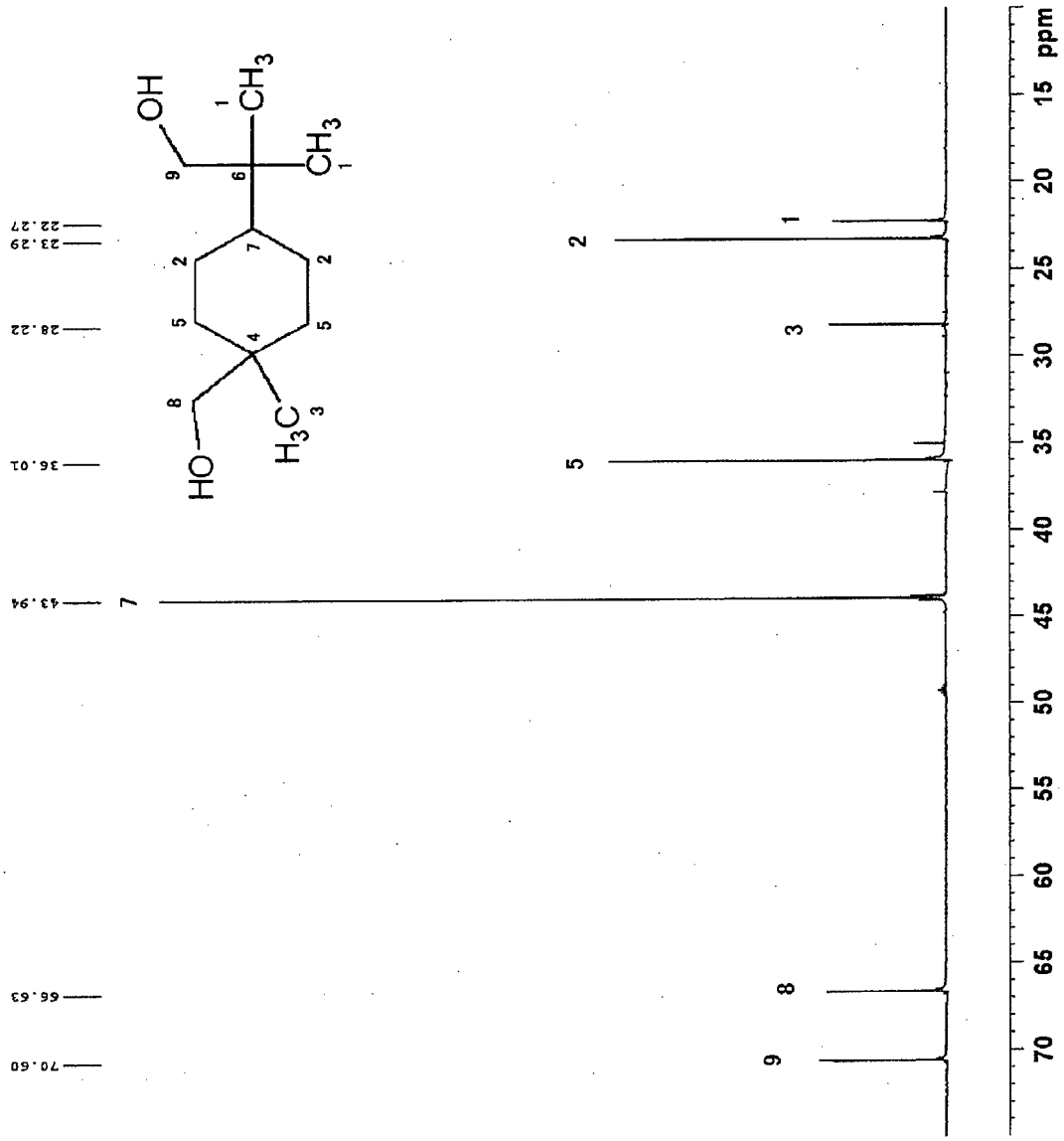
(4) (3) (2) (1)

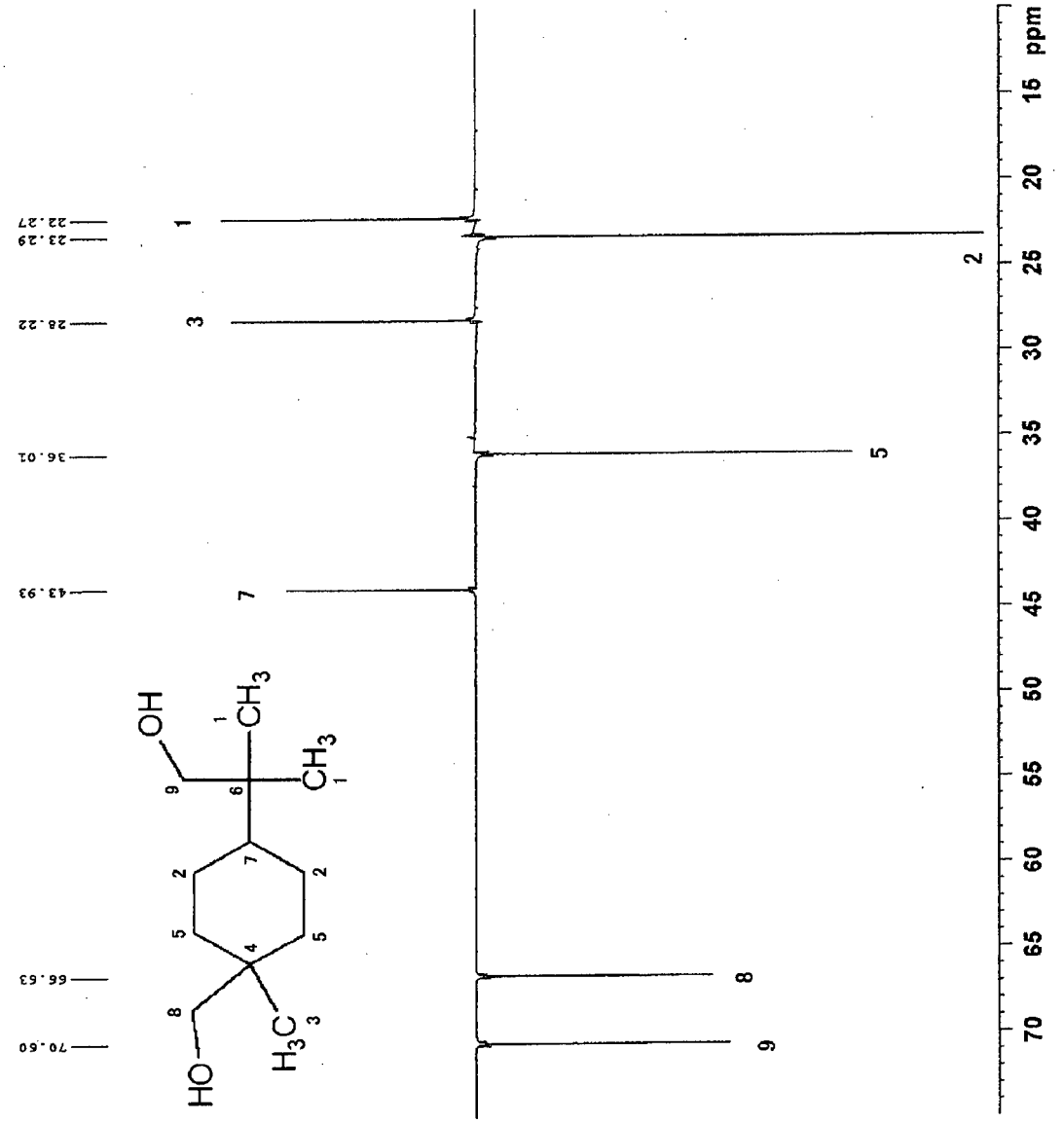
wherein R each independently represent an alkyl group having 1 to 4 carbon atoms.

[Fig. 1]


22.27
23.29
28.22
36.01
43.93
66.63
70.60
1
2
3
5
7
8
9
OH
CH3
CH3
HO
H3C
ppm
15
20
25
30
35
40
45
50
55
60
65
70

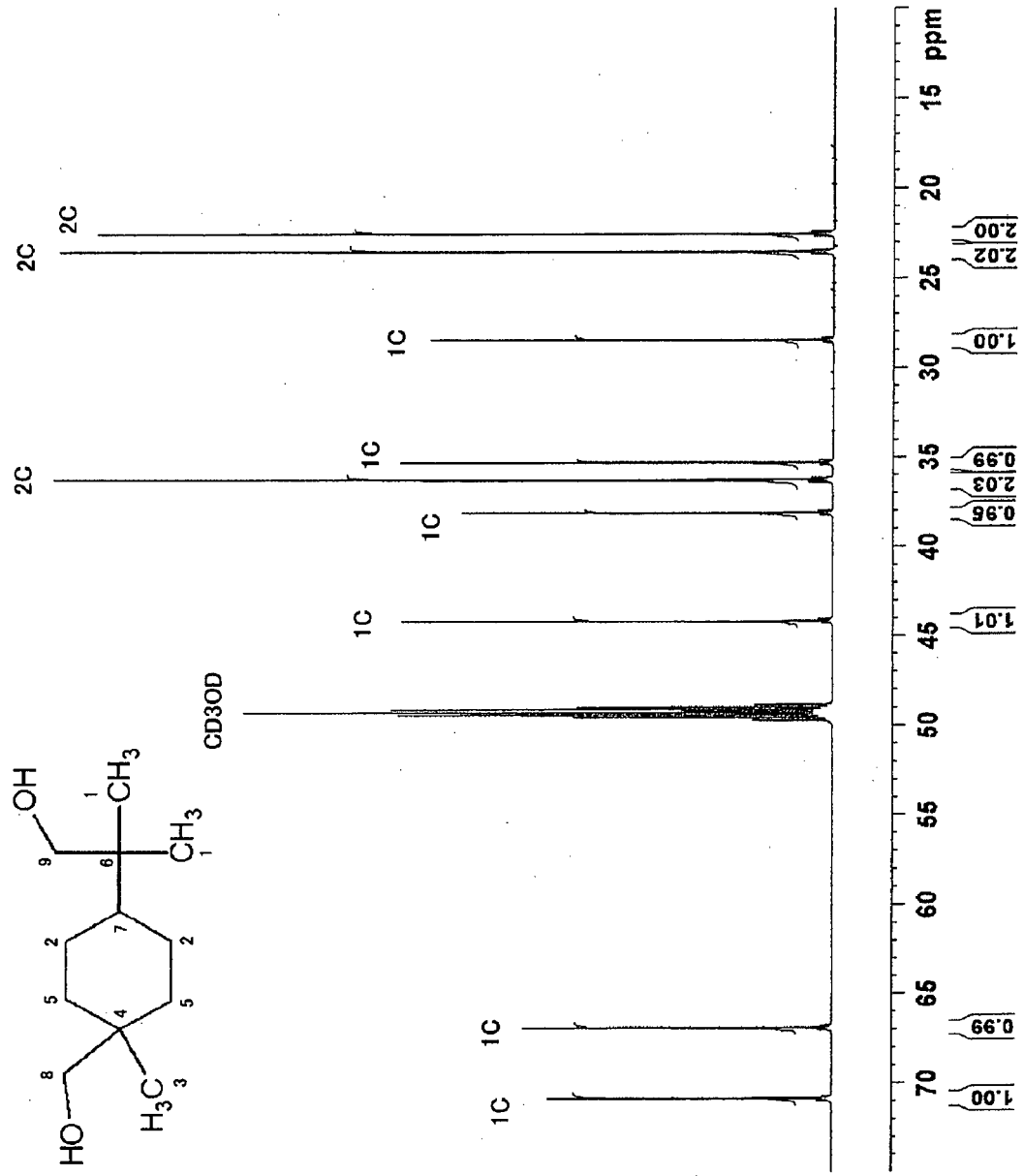
[Fig. 2]



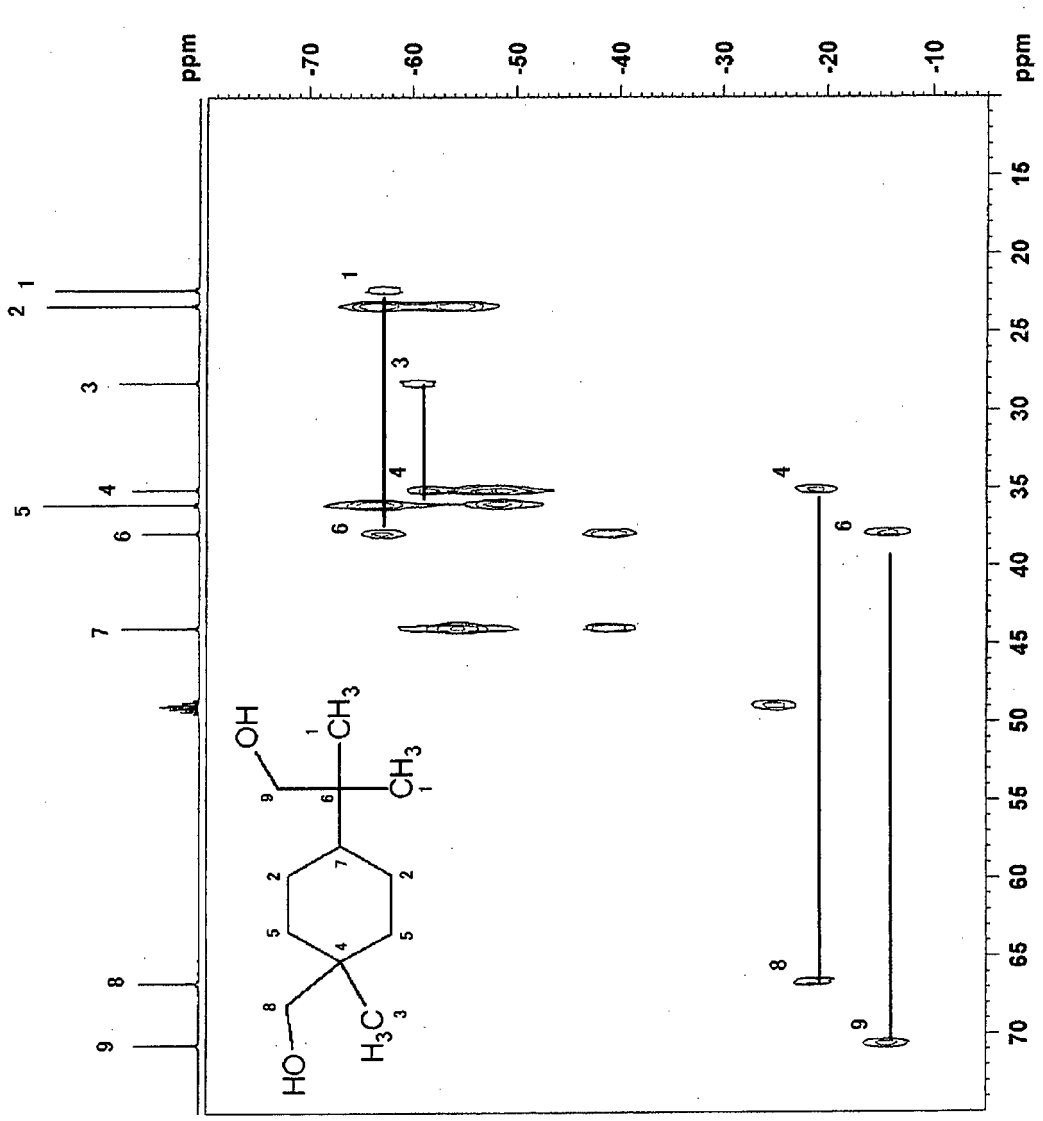

ppm
15
20
25
30
35
40
45
50
55
60
65
70
23.27
23.29
28.22
36.01
43.93
66.63
70.60
OH
CH3
CH3
HO
H3C

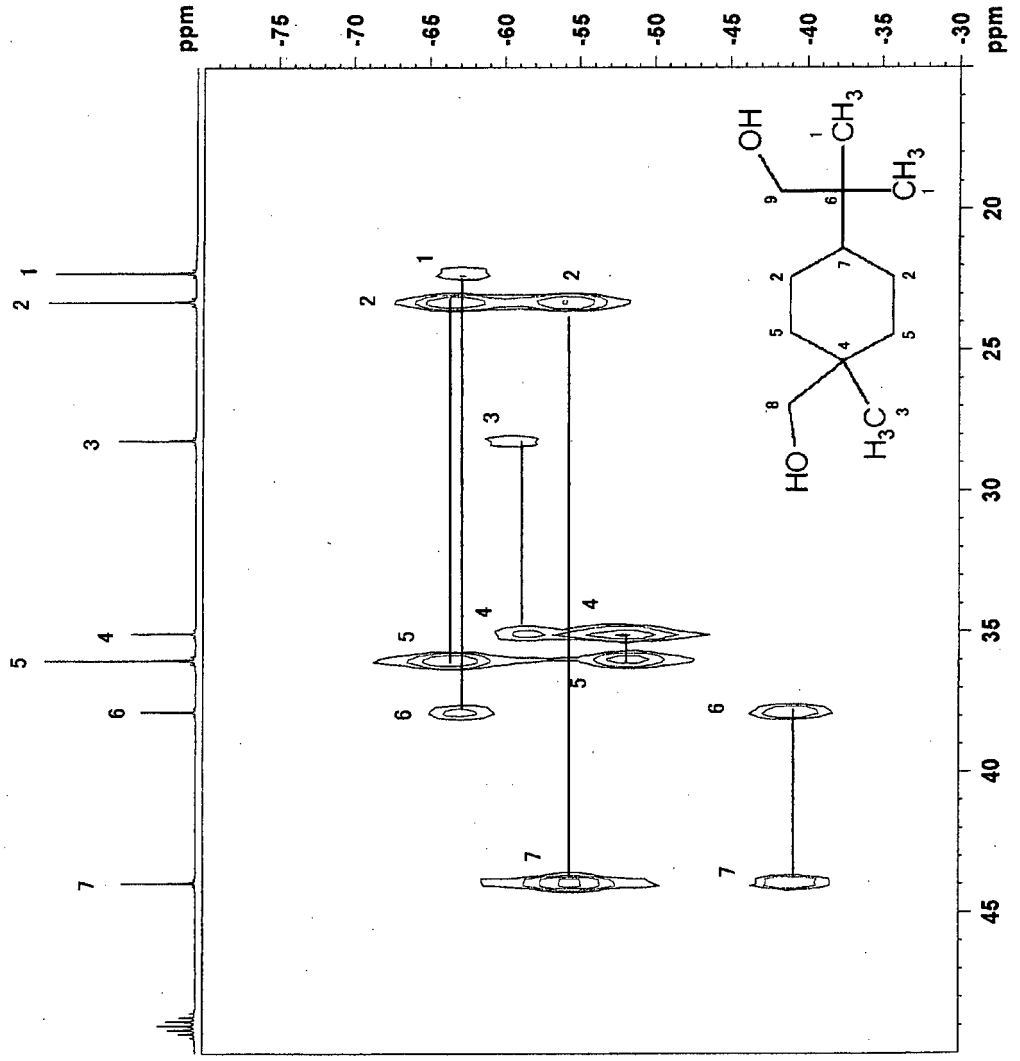
[Fig. 3]

[Fig. 4]


2C
2C
2C
1C
1C
1C
1C
CD3OD
1C
1C
OH
CH3
CH3
HO
H3C
ppm
15
20
25
30
35
40
45
50
55
60
65
70
2.00
2.02
1.00
0.99
2.03
0.96
1.01
0.99
1.00

[Fig. 5]


ppm
-70
-60
-50
-40
-30
-20
-10
ppm
15
20
25
30
35
40
45
50
55
60
65
70
OH
CH3
CH3
HO
H3C


ppm
-75
-70
-65
-60
-55
-50
-45
-40
-35
-30
ppm
20
25
30
35
40
45
OH
CH3
CH3
HO
H3C

[Fig. 6]

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/077710

A. CLASSIFICATION OF SUBJECT MATTER
C07C31/135(2006.01)i, *C07C29/149*(2006.01)i, *C07B61/00*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C31/135, C07C29/149, C07B61/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013
Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-521038 A (BASF SE), 21 July 2011 (21.07.2011), & US 2011/0040030 A1 & WO 2009/138387 A1	1-2
A	JP 2012-140354 A (Mitsubishi Gas Chemical Co., Inc.), 26 July 2012 (26.07.2012), & WO 2012/090977 A1	1-2
A	JP 2009-149577 A (Kao Corp.), 09 July 2009 (09.07.2009), (Family: none)	1-2
A	WO 2007/110978 A1 (Yasuhara Chemical Co., Ltd.), 04 October 2007 (04.10.2007), (Family: none)	1-2

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 December, 2013 (02.12.13)	10 December, 2013 (10.12.13)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/077710

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/138747 A1 (V. MANE FILS), 10 November 2011 (10.11.2011), & JP 2013-532123 A & US 2013/0123548 A1	1-2
A	US 2986584 A (American Cyanamid Co.), 30 May 1961 (30.05.1961), (Family: none)	1-2

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2000290356 A **[0004]**
- JP 2004124022 A **[0004]**
- JP 2005298555 A **[0004]**
- JP 3862538 B **[0004]**

Non-patent literature cited in the description

- The Fifth Series of Experimental Chemistry. Maruzen, vol. 14, 11-27 **[0027]**